

DIRECT METHANOL FUEL CELL SYSTEMS FOR FUTURE FORCE WARRIORS: FROM EXPERIMENTAL AND SIMULATIONS FOR WATER AND METHANOL CROSSOVER AND RECYCLING TO HIGH PERFORMANCE FUEL CELL SYSTEMS

Deryn Chu⁽¹⁾, Rongzhong Jiang⁽¹⁾, Scott Feldman⁽²⁾, Joseph Kowal⁽³⁾, and Dave Schimmel⁽⁴⁾

⁽¹⁾: United States Army Research Laboratory, Sensors and Electron Devices Directorate
2800 Powder Mill Rd. Adelphi, MD 20783-1197

⁽²⁾: United States Army Natick Soldier Research, Development and Engineer Center, Natick, MA

⁽³⁾: United States Army Communication Electronic Research, Development and Engineer Center, APG, MD

⁽⁴⁾: United States Army Program Executive Office Soldier, Project Manager Soldier Warrior, Fort Belvoir, VA

ABSTRACT

To produce a high power and high energy density direct methanol fuel cell (DMFC) system, it must use neat methanol as a fuel, and water produced at the cathode must be recycled. Based on Faradic reactions for DMFC, a series of theoretical equations over the entire discharge current ranges were explored and developed to model and simulate water and methanol crossover in a DMFC stack. The performance of the DMFC stack was then used to verify theoretical equations. The water and methanol crossover behavior of the DMFC system at different discharge currents was extensively investigated. The actual performance of the DMFC fuel cell stack agreed with the theoretical equations under a variety of experimental conditions. In addition to this modeling and lab-based work, a series of 20 watt DMFC systems are being developed under the Defense Acquisition Challenge Program (DACP) through the U. S. Army Program Executive Office (PEO) Soldier Project Manager Soldier Warrior (PM SWAR) team. The 20 watt DMFC systems were used in laboratory testing and in field exercises. The field exercises were supported by the Army Research Laboratory (ARL), Natick Soldier Research, Development and Engineer Center (NSRDEC), PEO Soldier and the U.S. Air Force Research Laboratory. The exercises explore the potential for using a small lightweight, high power and energy dense DMFC system for specific Soldier applications, such as for battery charging and hybrid power.

1. INTRODUCTION

The Army's Transformation demands a more responsive, deployable, agile, versatile, lethal, survivable, and sustainable force. This transformation will result in a Future Force, which will require power for highly mobile vehicles, unattended ground networked sensors, and individual Warfighters. The individual Warfighter requires extremely lightweight, quiet, efficient, and reliable power sources for a variety of portable electronics and other applications in the modern battlefield. DMFC is being evaluated as a potential portable power supply device to meet the requirements of future Soldier missions. The primary reason is its

relative safety, lightweight and high power and high energy density. DMFC technology to be used for future for Warriors includes: 1) small direct power units for unattended ground networked sensors; 2) medium power systems for an individual Warfighters; and 3) large power systems for command center, robotics, vehicles and future combat system of systems applications.

In this paper, we only address details related to DMFC stack power performance characteristics surrounding a set of medium power DMFC systems for the individual Warfighter. Using a lightweight DMFC system as the portable power source for the individual Soldier can reduce the overall weight burden on the carrier for certain missions. There are several key areas that need to be addressed to successfully produce the desired a high-performance and lightweight DMFC system: (1) methanol and water management, (2) thermal and heat transfer management, (3) environmental factors, (4) determination of the optimum stoichiometry of fuel and oxidant, and (5) system integration and balance of plant for high-performance DMFCs. All of these issues become simpler if we can use a series of theoretical equations to express the fuel cell reactions and performance.

All of the research papers published in the literature describes a single cell performance effect by methanol crossover work [Chu,D., Gilman S., 1994, Ren, X. M., 2000, Jiang, R. Z., 2004, Gurau, B., Smotkin, E. S. 2002, Wang, C. Y., 2005, 2007]. In the present study, we have explored and developed a series of theoretical equations to calculate water/methanol crossover and to understand the performance of a DMFC stack at different discharge current densities. This work addresses the progression from mathematical modeling of the performance of a DMFC stack through verification by laboratory testing and field exercises. The ultimate goal for this effort is to develop a highly efficient DMFC system for future Warrior applications.

2. Experimental

The basic DMFC consists of (a) an anode (platinum-ruthenium black), (b) an electrolyte (Nafion), and (c) a cathode (platinum black). A more detailed schematic of a

Report Documentation Page				Form Approved OMB No. 0704-0188	
Public reporting burden for the collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to a penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.					
1. REPORT DATE DEC 2008		2. REPORT TYPE N/A		3. DATES COVERED -	
4. TITLE AND SUBTITLE Direct Methanol Fuel Cell Systems For Future Force Warriors: From Experimental And Simulations For Water And Methanol Crossover And Recycling To High Performance Fuel Cell Systems				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S)				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) United States Army Research Laboratory, Sensors and Electron Devices Directorate 2800 Powder Mill Rd. Adelphi, MD 20783-1197				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release, distribution unlimited					
13. SUPPLEMENTARY NOTES See also ADM002187. Proceedings of the Army Science Conference (26th) Held in Orlando, Florida on 1-4 December 2008, The original document contains color images.					
14. ABSTRACT					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT SAR	18. NUMBER OF PAGES 8	19a. NAME OF RESPONSIBLE PERSON
a. REPORT unclassified	b. ABSTRACT unclassified	c. THIS PAGE unclassified			

single cell is shown in the Figure 1. The theoretical thermodynamic potential for a single methanol/air fuel cell is 1.21 V at ambient pressure (1 Atmosphere) and temperature (22°C).

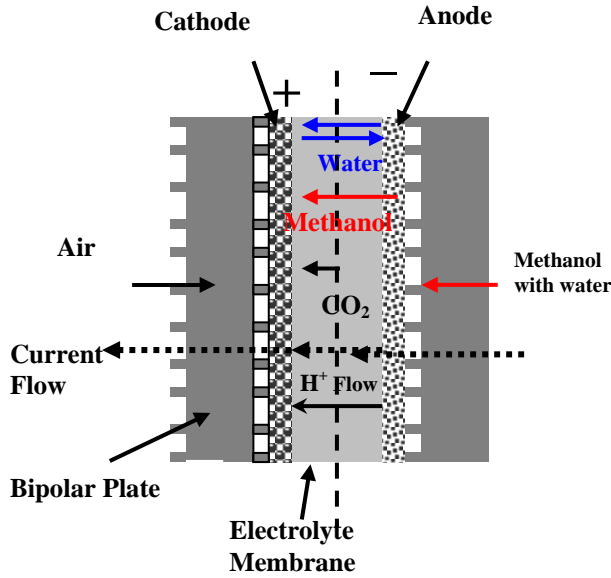


Figure 1 Water and methanol flow in a single cell unit in direct methanol fuel cell stack.

2.1 DMFC Stack

The DMFC stack, used for the research, contains 24 single cells, and each cell had an electrode of 20 cm². These single cells were assembled with graphite bipolar plates. The operating temperature of the DMFC stack was maintained by controlling the fuel temperature. The fuel was kept circulating through the anode of the stack.

2.2 Experimental Setup

A fuel circulation design was used to measure water and fuel crossover in a DMFC stack. The fuel was circulated to the anode of the DMFC stack through a fuel pump, and returned back to the fuel container. The whole circulation line was sealed, except that there is a pin-hole on a Teflon membrane at the top of the fuel container for release of the produced CO₂ that results from methanol oxidation at the anode. The water and fuel could not be released through the CO₂ vent, because of the hydrophobic nature of the Teflon membrane. The fuel flow rate was 114 ml/min, at which the DMFC stack could achieve the highest performance. Before carrying out the experiment, pure water was filled into the anode of the stack and the fuel circulation line, in order to accurately determine the volume of water and fuel in the fuel container.

Compressed dry air was used to feed the cathode of the DMFC stack. The air flow rate was 4 standard liters per minute (SLPM). The produced water was collected with a water container at the cathode outlet. The water

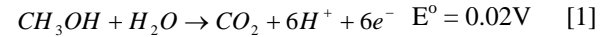
container was sealed with a pin-holed Teflon membrane at the top of the water container. The exhausted air at the cathode can be released through the pin-holes, but water release is limited through the pin-holed Teflon membrane.

Constant voltage discharge was carried out with a fuel cell test station. The methanol concentration was measured before and after the discharge. During operation time the fuel concentration was gradually decreased. A gravimetric method was used to determine the fuel concentrations. A standard curve of methanol concentration versus weight of 50 ml methanol solution was made at 22°C. A 50 ml sample of fuel was taken and weighed at the same temperature as that of making the standard curve. The methanol concentration was obtained by comparing the weight of the fuel with that of the standard curve.

2.3 Explore and Develop Theoretical Equations

Electrochemical oxidation of methanol and reduction of oxygen in DMFC stack are described as follows:

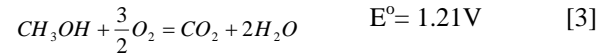
At the anode



At the cathode



Overall reaction is



The Faradic efficiency (ζ), energy efficiency (η) and energy density (ε , Wh/kg) for methanol electrochemical oxidation in a DMFC stack can be expressed as:

$$\zeta = \frac{3600NC_{\text{apend}}}{nF(V_{a1}C_1 - V_{a2}C_2)} \quad [4]$$

Here, N is cell number in DMFC stack; n is number of electrons in methanol oxidation; C_{apend} (Ah) is discharge capacity of the DMFC stack at the end of operating time; F is Faradic constant; V_{a1} and V_{a2} are fuel volumes (liter) in the anode fuel container at the beginning time and at the end time, respectively; C₁ and C₂ are methanol concentration (mol/L) in anode fuel container at the beginning time and at the end time, respectively.

$$\eta = \frac{\zeta E}{1.21N} \quad [5]$$

Here, E is discharge voltage (V); the number 1.21 is theoretical voltage of a single DMFC.

$$\varepsilon = \frac{1.21nF\eta}{3.6M_{\text{MeOH}}} \quad [6]$$

Here, M_{MeOH} is molecular weight of methanol.

The water weight produced by Faradic reaction and collected at cathode water container ($W_{H_2O_{MeOHf}}$, g) is given by:

$$W_{H_2O_{MeOHf}} = \frac{3600C_{apt}NM_{H_2O}}{2F} \quad [7]$$

Here, C_{apt} (Ah) is discharge capacity of DMFC stack at the time t . The methanol weight oxidized at anode by Faradic reaction (W_{MeOHf} , g) is given by:

$$W_{MeOHf} = \frac{3600C_{apt}NM_{MeOH}}{nF} \quad [8]$$

The methanol weight permeated across the membrane (W_{MeOHcr} , g) is given by:

$$W_{MeOHcr} = \frac{W_{MeOHf}(1-\zeta)}{\zeta} \quad [9]$$

If a DMFC stack is under open circuit condition, the methanol weight permeated across the membrane can be calculated by:

$$W_{MeOHcr} = (V_{a1}C_{a1} - V_{a2}C_{a2})M_{MeOH} \quad [9b]$$

The methanol concentration at time t (C_{MeOH} , mol/L) is given by:

$$C_{MeOH} = \frac{V_{a1}C_{a1} - (W_{MeOHf} + W_{MeOHcr})/M_{MeOH}}{V_t} \quad [10]$$

Here, V_t is fuel volume (liter) in the anode fuel container at time t . The water production caused by methanol crossover ($W_{H_2O_{MeOHcr}}$, g) is given by:

$$W_{H_2O_{MeOHcr}} = \frac{2M_{H_2O}W_{MeOHcr}}{M_{MeOH}} \quad [11]$$

The theoretical total water produced and permeated (W_{thH_2O}) can be calculated. Because W_{thH_2O} is equal to the total material weight loss at anode container minus the weight loss by (reacted methanol + crossed over methanol) and plus the water weight produced by the (reacted methanol + crossed over methanol). Therefore, we have:

$$W_{thH_2O} = 1000(V_{a1} - V_{a2})d - (W_{MeOHf} + W_{MeOHcr}) + \frac{2M_{H_2O}(W_{MeOHf} + W_{MeOHcr})}{M_{MeOH}} \quad [12]$$

$$W_{thH_2O} = 1000(V_{a1} - V_{a2})d + \frac{(W_{MeOHf} + W_{MeOHcr})}{8} \quad [13]$$

Here, d is fuel density (kg/L). Water evaporated at the cathode container ($W_{H_2O_{vapor}}$, g) can be expressed as:

$$W_{H_2O_{vapor}} = W_{thH_2O} - W_{H_2O_{exp}} \quad [14]$$

Here, $W_{H_2O_{exp}}$ (g) is water amount experimentally collected at the cathode container.

The water permeated across membrane ($W_{H_2O_{cross}}$, g) is given by:

$$W_{H_2O_{cross}} = W_{thH_2O} - W_{H_2O_{MeOHf}} - W_{H_2O_{MeOHcr}} \quad [15]$$

Water permeating across the membrane can be split into three portions, including proton osmotic-drag, methanol migration-drag, and spontaneous water crossover.

$$W_{H_2O_{cross}}(MeOH - drag) = W_{H_2O_{cross}}(OCV) - W_{H_2O_{cross}}(Pure - water) \quad [16]$$

$$W_{H_2O_{cross}}(H^+ - drag) = W_{H_2O_{cross}} - W_{H_2O_{cross}}(OCV) \quad [17]$$

Here, $W_{H_2O_{cross}}(MeOH-drag)$ and $W_{H_2O_{cross}}(H^+-drag)$ are the amounts of water crossover caused by methanol migration-drag and proton osmotic drag, respectively. $W_{H_2O_{cross}}(OCV)$ is the experimentally measured water crossover at open circuit condition, which is the sum of water crossover caused by methanol migration-drag and spontaneous water permeation. $W_{H_2O_{cross}}(pure-water)$ is the amount of spontaneous water crossover, which is experimentally measured by using pure water to replace methanol solution in the DMFC stack.

3. Results and Discussion

There are three different types of water crossover across the electrolyte membrane in a DMFC stack, including spontaneous water crossover, methanol migration-dragged water crossover, and proton osmotic-dragged water crossover.

3.1 Determination of Water Spontaneous Crossover

The first type of water crossover is spontaneous, even without any power load. In order to determine the amount of each type of water crossover, we need to first measure the spontaneous water crossover. Table 1 below lists water crossover results obtained by circulating pure water in a DMFC stack at an operating temperature of 62°C. The experimental results demonstrated that even if no fuel existed in the fuel container and no current passed in the fuel cell stack, there is still a significant amount of water (111.0g) collected at the cathode water container. The collected water in the cathode water container must result from the spontaneous water crossover across the electrolyte membrane. Because the total water loss in the fuel container is 137g, the evaporated water is 26g calculated with Eq (14). The normalized spontaneous water crossover rate is 1.186 $\text{mg} \cdot \text{min}^{-1} \cdot \text{cell}^{-1} \cdot \text{cm}^{-2}$. The water evaporation rate is 27.02

$\text{mg}\cdot\text{min}^{-1}\cdot\text{L}^{-1}$ for circulating pure water at 62°C with air flow rate 4 SLPM. The water evaporating rate is relevant to the air flow rate and the temperature difference between the DMFC stack and the cathode water container.

Table 1 Water crossover results obtained by circulating pure water in a DMFC stack at operating temperature 62°C .

Parameter Specifications	Experimental results
Water collected at cathode w container (g)	111.0
Total water permeated across membrane (g)	137.0
Water evaporated from cathode water container (g)	26.0
Water spontaneous crossover ($\text{mg}\cdot\text{min}^{-1}\cdot\text{cell}^{-1}\cdot\text{cm}^{-2}$)	1.186
Water evaporation rate brought by air ($\text{mg}\cdot\text{min}^{-1}\cdot\text{L}^{-1}$ air)	27.02

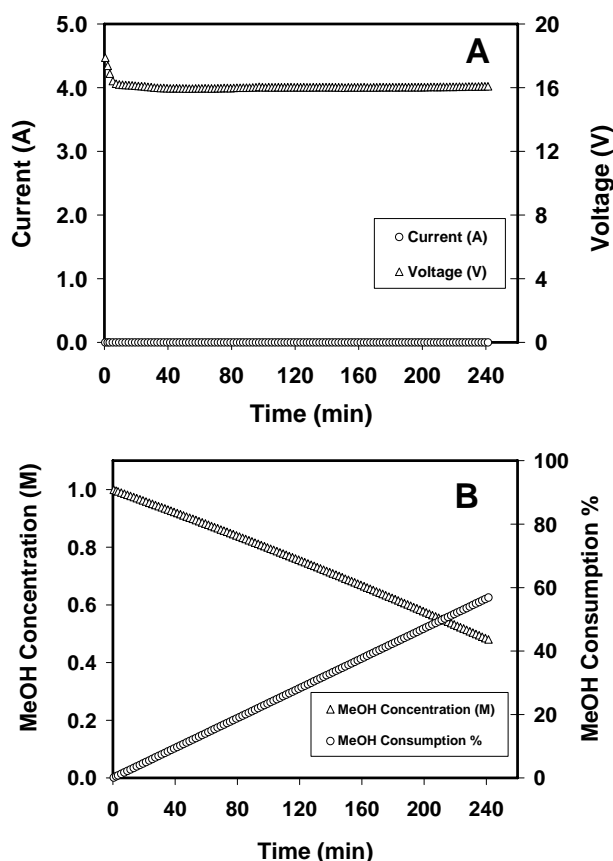


Figure 2 (A) Voltage and current versus time; (B) methanol concentration and percentage of methanol consumption versus time in a DMFC stack. 1.0M methanol at 62°C .

3.2 Determination of Water Crossover Dragged by Methanol Migration.

The second type of water crossover is dragged by methanol migration. Water crossover rate dragged by methanol migration can be expressed with Eq (16) by analysis of the experimental results of a DMFC stack under open circuit condition. Figure 2A and 2B show plots of stack voltage and methanol concentration versus time for a DMFC stack under open circuit condition at 60°C by circulating methanol solution with starting of 1.0M, respectively.

Table 2 Water crossover results obtained from circulating 1.0M methanol in a DMFC stack under open circuit condition at operating temperature 62°C .

Parameter Specifications	Experimental results
Methanol crossed over ($\text{mg}\cdot\text{min}^{-1}\cdot\text{cell}^{-1}\cdot\text{cm}^{-2}$)	0.315
Water produced by direct methanol oxidation at cathode ($\text{mg}\cdot\text{min}^{-1}\cdot\text{cell}^{-1}\cdot\text{cm}^{-2}$)	0.354
Total water crossover rate ($\text{mg}\cdot\text{min}^{-1}\cdot\text{cell}^{-1}\cdot\text{cm}^{-2}$)	1.43
Water dragged by methanol migration ($\text{mg}\cdot\text{min}^{-1}\cdot\text{L}^{-1}$ air)	0.243

The stack voltage is almost at 16V, but the methanol concentration decreases continuously. After 4 hour runtime, the methanol concentration decreased to 0.48M, and 57% methanol was consumed. Apparently, there is a significant amount of methanol crossover even at open circuit. In addition, water crossover and water production can be observed by a significant decrease of fuel volume in the anode fuel container, and by a significant increase of water collected in the cathode water container. Table 2 lists water crossover results obtained from circulating 1.0M methanol in a DMFC stack under open circuit condition at an operating temperature of 62°C . As 1.0M methanol is added to the fuel container, the collected water increases in the cathode water container, and water permeation rate also correspondently increases from $1.186 \text{ mg}\cdot\text{min}^{-1}\cdot\text{cell}^{-1}\cdot\text{cm}^{-2}$ to $1.43 \text{ mg}\cdot\text{min}^{-1}\cdot\text{cell}^{-1}\cdot\text{cm}^{-2}$. Therefore, $0.243 \text{ mg}\cdot\text{min}^{-1}\cdot\text{cell}^{-1}\cdot\text{cm}^{-2}$ of water crossover rate was dragged by methanol. The methanol crossover rate can be calculated with Eq (9b). As shown in Table 2, the normalized methanol crossover rate across the electrolyte membrane is $0.315 \text{ mg}\cdot\text{min}^{-1}\cdot\text{cell}^{-1}\cdot\text{cm}^{-2}$, and the corresponding water production rate caused by the methanol oxidation at the cathode is $0.354 \text{ mg}\cdot\text{min}^{-1}\cdot\text{cell}^{-1}\cdot\text{cm}^{-2}$ under the same operating condition (1.0M methanol, 62°C) described above.

3.3 Determination of Water Crossover Dragged by Proton Osmotic Migration

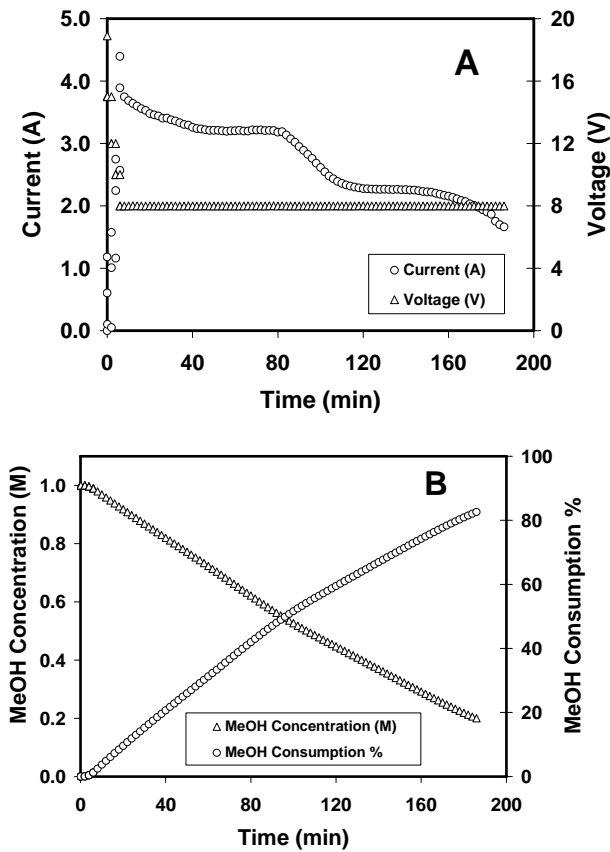


Figure 3 (A) Voltage and current versus time; (B) Methanol concentration and percentage of methanol consumption versus time in a DMFC stack. 1.0M methanol at 8.0V discharge at 62°C.

The third type of water crossover under discharge conditions is water crossover dragged by proton osmotic-drag. There are two ways of water production at the cathode in a DMFC: (1) water produced by methanol Faradic oxidation at the anode and oxygen Faradic reduction at the cathode to produce water; and (2) by direct chemical reaction between oxygen coming from the cathode and methanol crossed over from the anode. Therefore, total three ways of water permeation and two ways of water production are considered. According to equation (17), we can experimentally determine water crossover dragged by proton osmotic migration. Figure 3A and 3B show plots of discharge current and methanol concentration versus time under constant voltage discharge at 8.0V for a DMFC stack operated by circulating 1.0M methanol at 62°C, respectively. The discharge current fluctuates slightly because the internal stack temperature deviates from the programmed value, which is caused by an additional heat generation from methanol crossover. Apparently, the internal DMFC stack's temperature is more difficult to be controlled than that of a single cell if higher concentration of methanol is used. The experimental temperature deviation measured

was $\pm 2^\circ\text{C}$. With time continuing, the methanol is consumed gradually, which leads to a decrease of methanol concentration, and also the discharge current. About 80% methanol was consumed after 3 hour of running, and the methanol concentration was decreased from 1.0 to 0.2M. The water crossover dragged by proton osmotic migration can be calculated from the data of the two experiments under open circuit and under constant voltage discharges.

Table 3 lists water and fuel crossover results obtained from circulating 1.0M methanol in a DMFC stack at operating temperature 62°C under various discharge voltages. The methanol crossover rate increases with increasing discharge voltage. For stack voltages 8.0, 9.0 and 10.0V, the methanol crossover rates are 0.143, 0.143 and 0.152 $\text{mg}\cdot\text{min}^{-1}\cdot\text{cell}^{-1}\cdot\text{cm}^{-2}$, respectively. On the contrary, the water crossover rate decreases with increasing discharge voltage. For stack voltages 8.0, 9.0 and 10.0V, the water crossover rates are 2.090, 1.568, and 1.781 $\text{mg}\cdot\text{min}^{-1}\cdot\text{cell}^{-1}\cdot\text{cm}^{-2}$, respectively.

Table 3. Water and fuel crossover results obtained from circulating 1.0M methanol in a DMFC stack under constant voltage discharge at operating temperature 62°C.

Parameter Specifications	Stack Discharge Voltage		
	8.0V	9.0V	10.0V
Methanol crossed over ($\text{mg}\cdot\text{min}^{-1}\cdot\text{cell}^{-1}\cdot\text{cm}^{-2}$)	0.143	0.143	0.152
Water crossover rate ($\text{mg}\cdot\text{min}^{-1}\cdot\text{cell}^{-1}\cdot\text{cm}^{-2}$)	2.090	1.586	1.781
Water evaporation rate ($\text{mg}\cdot\text{min}^{-1}\cdot\text{L}^{-1}\cdot\text{air}$)	47.86	50.03	56.53

With increasing discharge voltage, the water production rate caused by methanol Faradic reaction decreases, but the one caused by direct methanol chemical oxidation at the cathode increases. Figure 4 shows effect of stack voltage on water crossover rate. The rate of H^+ -osmotic dragged water crossover decreases with increasing discharge voltage. For stack voltages 8.0 and 10.0V, the H^+ -osmotic dragged water crossover rates are 0.661 and 0.352 $\text{mg}\cdot\text{min}^{-1}\cdot\text{cell}^{-1}\cdot\text{cm}^{-2}$, respectively. However, the rates of water spontaneous crossover and the methanol migration dragged water crossover do not change. The highest percentage of water amount collected in the cathode water container is caused by water spontaneous crossover. The secondary highest percentage is by methanol Faradic oxidation.

3.4 Faradic Efficiency, Energy Efficiency and Energy Density

Table 4 lists Faradic efficiency, energy efficiency and energy density of a DMFC stack at operating temperature 62°C under various discharge voltages. The

Faradic efficiency decreases, but energy efficiency increase with increasing discharge voltage. At 10.0V or cell voltage 0.417V, the highest energy density is obtained (1381Wh/Kg of methanol). The energy efficiency is not only dependent on Faradic efficiency, but also dependent on cell voltage.

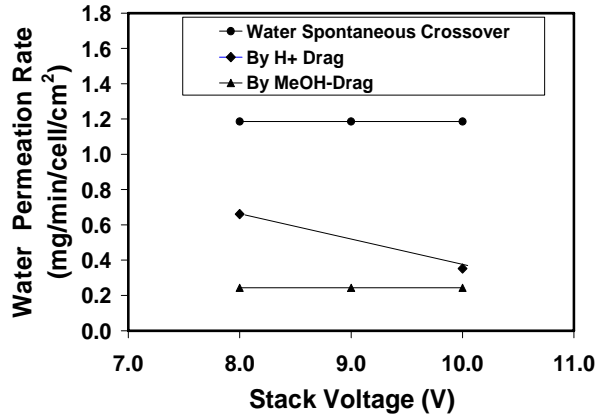


Figure 4 Effect of stack voltage on water permeation rates. Methanol concentration: 1.0M. Operating temperature at 62°C.

Table 4 Faradic efficiency, energy efficiency and energy density of a DMFC stack under constant voltage discharge at operating temperature 62°C.

Parameter Specifications	Stack Discharge Voltage		
	8.0V	9.0V	10.0V
Cell Voltage (V)	0.333	0.3750	0.417
Faradic Efficiency	0.756	0.702	0.659
Energy Efficiency	0.208	0.218	0.227
Energy Density (Wh/kg)	1267	1324	1381

3.5 Effect of Operating Temperature

Operating temperature significantly affects water and fuel crossover, as well as Faradic efficiency, energy efficiency and energy density. Table 5 lists water and fuel crossover results obtained from circulating 1.0M methanol in a DMFC stack under constant voltage (8.0V) discharge at various operating temperatures. As shown in the Figure 5, with increasing operating temperature, both water crossover and methanol crossover rates increase. For temperatures 27, 42 and 62°C, the methanol crossover rates are 0.034, 0.084 and 0.143 mg·min⁻¹·cell⁻¹·cm⁻²; and the water crossover rates are 0.324, 0.722, and 2.090 mg·min⁻¹·cell⁻¹·cm⁻², respectively. It is interesting that the water evaporation rate increases, but the percentage of water evaporation decreases with increasing operating temperature. For example, at 27, 42 and 62°C, the water evaporation rates are 16.51, 28.23 and 47.86 mg·min⁻¹·L⁻¹ air; but the percentages of water evaporation are 20.60, 17.60 and 13.26%, respectively. The percentage of water evaporation is dependent on the temperature differences between the DMFC stack and

the cathode water container. The higher the temperature difference, the more percentage of water can be cooled down in the cathode water container. Apparently, we cannot 100% recycle the cathode water in a DMFC stack or a DMFC system.

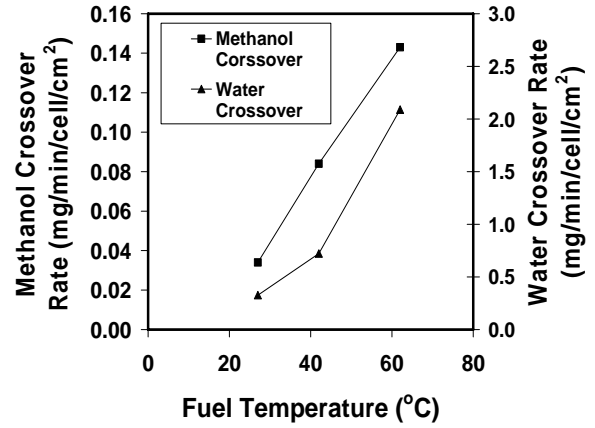


Figure 5 Effect of temperatures on water and methanol crossover. Stack voltage: 8.0V. Methanol concentration: 1.0M.

Table 5 Water and fuel crossover results obtained from circulating 1.0M methanol in a DMFC stack under constant voltage discharge at various operating temperatures.

Parameter Specifications	Stack Discharge Voltage		
	27°C	42°C	62°C
Methanol crossed over (mg·min ⁻¹ ·cell ⁻¹ ·cm ⁻²)	0.034	0.084	0.143
Water crossover rate (mg·min ⁻¹ ·cell ⁻¹ ·cm ⁻²)	0.327	0.722	2.090
Water evaporation rate (mg·min ⁻¹ ·L ⁻¹ air))	16.51	28.23	47.86

Table 6 lists Faradic efficiency, energy efficiency and energy density of a DMFC stack under constant voltage (8V) discharge at various operating temperatures. With increasing temperature, both Faradic efficiency and energy efficiency decrease. For operating temperature 27, 42 and 62, the energy densities are 1405, 1316 and 1267Wh/kg of methanol, respectively. The lowest operating temperature turned out to give the highest energy density.

3.6. Simulation of Water Recycling

The obtained water crossover data from the model DMFC stack was used to simulate a 20 W DMFC system, and calculate the variations of fuel concentration in the anode water tank under various water recycling percentages and operating conditions.

Table 6. Faradic efficiency, energy efficiency and energy density of a DMFC stack under constant voltage (8.0V) discharge at various operating temperatures.

Parameter Specifications	Stack Discharge Voltage		
	27°C	42°C	62°C
Faradic Efficiency	0.839	0.786	0.756
Energy Efficiency	0.231	0.216	0.208
Energy Density (Wh/kg)	1405	1316	1267

If too much water is recycled in the anode water tank, the methanol concentration will be lower than the optimum value for a DMFC system that recycles the cathode water. Alternatively, if too little water is recycled in the anode water tank, the methanol concentration will be too high. Too high a methanol concentration may cause severe damage to the catalyst layer of the DMFC stack. Therefore, an optimum percentage of recyclable water is required to maintain a desired methanol concentration. Figure 6A shows variations of methanol concentration with time by recycling different percentages of recyclable water for a 20 W DMFC system with an average cell voltage of 0.42 V and at an operating temperature of 62°C. In this simulation, we assume that the desired methanol concentration is 1.0 M, and the initial solution volume in the anode water tank is 100 mL. Surprisingly, we need to recycle 98% of the water to maintain methanol concentration to be 1.0 M. If water recycling is lower than 90%, the methanol concentration will reach 1.6 M within 6 hours of operation. If water recycling is lower than 80%, the methanol concentration will rise to above 3.5 M by 5 hours.

Figure 6B shows plots of corresponding solution volume versus time for the same operating conditions as that described in Figure 6A. Apparently, the change of methanol concentration with time is attributed to variations of the solution volume that is directly linked to water recycling percentage.

Figure 7A and 7B below show the effects of the water recycling percentage on methanol concentration in an anode water tank for a 20 W DMFC system with 180 min of operation. The best balance of water consumption, generation, and recycling for average cell voltages at 0.42 V needs to recycle 98% water; but for an average cell voltage of 0.33 V, 90% water needs to be recycled. If the water recycling percentage is more than needed, the water level in the anode water tank will be increased, and the methanol concentration will be decreased. Alternatively, if the amount of water recycling is less than needed, the water level in the anode water tank will be decreased, and the methanol concentration will be increased.

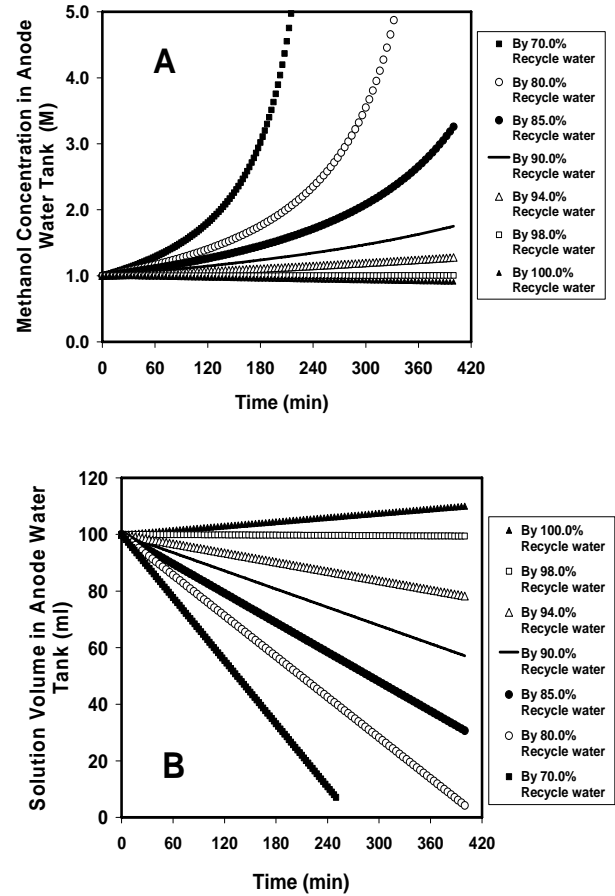


Figure 6 (A) Methanol concentration versus time; (B) Solution volume versus time in anode water tank for a 20W DMFC system by recycling cathode water. Volume of initial solution in anode water tank: 100 ml 1.0M methanol. Average cell voltage of stack: 0.42V. Operating temperature: 62°C.

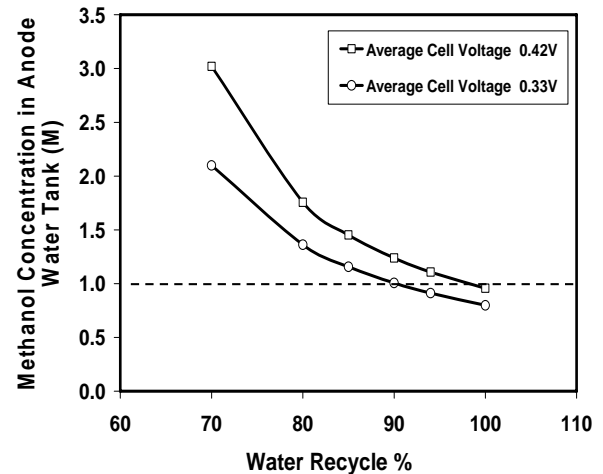


Figure 7 Effect of water recycling % on methanol concentration in anode water tank for a 20W DMFC system by 180 min running.

4. THE FIELD EXERCISES

A series of different prototype 20 watt DMFC systems (M-25 Alpha I, M-25-Beta and M-25 final) are being developed under the Defense Acquisition Challenge Program (DACP) through the U. S. Army Program Executive Office (PEO) Soldier Project Manager Soldier Warrior. The DMFC systems are also evaluated at the Army research Laboratory and tested in the field. During the final year (2007) of the Future Force Warrior (FFW) Advanced Technology Demonstration (ATD) program, managed by the Natick Soldier Research, Development and Engineering Center (NSRDEC), M-25 Alpha I prototype DMFC systems, fabricated by and DuPont and Smart Fuel Cell (SFC) AG, were field tested by the Army at two locations: Ft. Dix, NJ and Ft. Benning, GA. The Ft. Dix tests were conducted within the Army's C4ISR On-The-Move developmental test venue from July 20-25, 2007. The Ft. Benning tests were conducted as part of the AAEF Spiral D Ground Soldier Systems operational test event from October 22 to November 5, 2007. An M-25 Beta prototype DMFC system was tested in Iraq by PM SWAR personnel for battery charging applications in February 2008 (Fig. 8). The M-25 Beta and M-25 final systems performed very well for battery charging and power functions at ARL facilities in February to September 2008.



Figure 8 An M-25 Beta DMFC system evaluated in Iraq

Based upon current demonstrations, tests, and exercises, it is projected that a small lightweight, high power and energy DMFC system is a potentially viable option for specific Soldier applications, such as for battery charging and hybrid power.

5. CONCLUSIONS

Water and fuel crossover in a direct methanol fuel cell (DMFC) stack under various operating conditions was quantitatively determined by a method of mass balance analysis of fuel and water. With increasing discharge voltage, fuel crossover rate increases, but water crossover decreases slightly. With increasing operating temperature, both water and fuel crossover rates increase significantly. There are three types of water crossover, including proton osmotic-drag, methanol migration-drag, and water spontaneous crossover. Among them, water spontaneous crossover is the most significant. Water crossover and evaporation result in great challenges for a DMFC system to recycle the cathode water. The rate of methanol crossover increases significantly with operating temperature, but only slightly with increasing discharge voltage. With

increasing operating temperature, both Faradic efficiency and energy efficiency decreases. Higher energy density is obtained at lower operating temperature and relatively higher cell voltage (0.42V) for a DMFC stack.

To use pure methanol as a fuel, a DMFC system must recycle the cathode water. The variations of methanol concentration and solution volume with operating time in a 20 W DMFC system that recycles the cathode water were simulated. Methanol concentration and solution volume can be kept constant by long term operation of a DMFC system, as long as an appropriate amount of water is recycled and maintained under a specific operating condition.

Understanding the performance characteristics of the DMFC stack is clearly important for realizing the optimum cost/weight/volume/performance ratios. The results of this study advance the development of the DMFC system for practical use by future Warriors.

ACKNOWLEDGEMENTS

This work received the Army 2008 Research and Development Award. The authors wish to thank the Department of the Army and the Army Materiel Command (AMC) for their financial support. Under a joint technology planning annex (TPA), fuel cell groups at the ARL, the CERDEC, the NSRDEC and PEO Soldier Project Manager Soldier Warrior worked together to develop Army power sources for Future Force Warrior (FFW) testing and future Ground Soldiers systems applications.

REFERENCES

- Chu, D., Gilman, S., 1994: The influence of methanol on O_2 electroreduction at A rotating disk electrode in acid electrolyte, *J. Electrochemical Society*, Volume, 141 (7), 1770-1773.
- Ren, X. M., Gottesfeld, S. J. 2000: Recent advances in direct methanol fuel cells at Los Alamos National Laboratory “, *J. Power Sources* 86 (1-2), 111-116.
- Jiang, R. Z., Rong, C., Chu, D., 2004: Determination of energy efficiency for a direct methanol fuel cell stack by a fuel circulation method. *J. Power Sources* 126 (1-2), 119-124.
- Gurau, B., Smotkin, E. S., 2000: Methanol crossover in direct methanol fuel cells: a link between power and energy density, *J. Power Sources*, 112 (2), 339-352.
- Ren, X., Gottesfeld, S., 2000: Water and methanol uptakes in Nafion membranes and membrane effects on direct methanol cell performance, *J. Electrochem. Soc.*, 147 (1), 92-98.
- Lu, G. Q., Liu, F. Q., Wang, C. Y., 2005: Water transport through Nafion 112 membrane in DMFCs, *Electrochem. Solid. Lett.*, 8 (1), A1-A4.
- Liu, W. P., Wang, C. Y., 2007: Modeling water transport in liquid feed direct methanol fuel cells, *J. Power Sources*, 164 (1), 189-195.